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14. ABSTRACT We have initiated a program in which charge exchange during low energy (0.5-5.0 keV) ion scattering is used to investigate emergent phenomena, such as superconductivity and the Kondo effect, at surfaces. Because of the localized nature of their interaction with solids, ions are one of the most useful probes of surface composition and atomic structure. It has also been demonstrated that the neutralization of scattered alkali (and certain other) ions is dependent on the local electronic configuration at the scattering site. We collect the energy spectra and charge-state					
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Low-Energy Ion Scattering as a Probe of Correlated Electrons at Surfaces

Final Project Report

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Statement of the problem studied

The incorporation of correlated electron phenomena into electronic devices is an important part of the effort to move technology beyond the limitations of silicon. Examples include conventional and high-temperature superconductors, Kondo systems, exotic magnetic systems, and colossal magnetoresistive materials. To fully exploit such phenomena, it is necessary to understand the fundamental physics and surface properties at the nanometer length scale.

We have initiated a program in which low energy (0.5-5.0 keV) ions are used to investigate emergent phenomena at surfaces. We probe the local surface potential and electronic configuration through measurements of charge exchange and electron emission that occur during scattering. Because of the localized nature of their interaction with solids, ions are one of the most useful probes of surface composition and atomic structure [1]. It has also been demonstrated that the inelastic interactions of ions with surfaces are sensitive to the local electronic configuration at the scattering site [2-8]. In particular, ion neutralization is enhanced when the local surface work function decreases, and is conversely reduced when the local work function increases. This enables low energy alkali ion neutralization to serve as a probe of the local surface potential on an inhomogeneous material.

For this abbreviated project, we applied the ion scattering technique to a few key correlated electron systems. We collected charge-state resolved time-of-flight spectra of the emitted atomic particles as a function of energy, angle and sample temperature. An analysis of the spectra provides the neutral fraction of alkali ions scattered from each particular atomic site on the surface. The neutralization is understood within the framework of the Resonant Charge Transfer (RCT) mechanism, which is applicable for any atomic particle with an ionization potential that overlaps states in the surface [9]. The neutral fraction depends on the local electrostatic potential, sometimes referred to as the local work function, above the scattering site. These measurements provide information on surface electronic structure that is not available with other tools.

Summary of the most important results

1) High temperature superconductors. Samples of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ high T_C material, or BSCCO, were investigated with low energy alkali ion scattering. (The material was provided by Genda Gu from Brookhaven National Laboratory.) Single crystal samples of BSCCO were cleaved in ultra-high vacuum, which produces uniform surfaces that are atomically flat. Previous surface studies have mainly been confined to scanning probe microscopy and photoemission [10-12]. Reports of ion beam experiments on cuprate materials that do exist have either focused on disorder-induced changes to the critical current [13], rather than surface physical and electronic structure,

or have been on surfaces that are much less ordered than cleaved BSCCO, such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [14]. We collected charge state-resolved spectra of low energy Li^+ and Na^+ ions scattered from BSCCO as a function of sample temperature, ion energy and impact angle, and adatom coverage.

The time-of-flight ion scattering spectra show one well-resolved single scattering peak, which demonstrates that the surface is terminated by a Bi-O layer while the other metallic atoms are positioned below the surface. This is the expected termination, based on the fact that two Bi-O layers are weakly bound to each other in the single crystal structure.

The Bi-O surface has an inhomogeneous surface potential due to the transfer of charge from Bi to the electronegative O atoms. This inhomogeneity is reflected in the angular dependence of the neutralization.

Although scanning probe measurements have shown that there are charge density rearrangements associated with the non-superconducting layers, we did not observe a measurable change in the ion scattering charge exchange as the sample was cooled below T_C .

We deposited electropositive, electronegative and neutral species (K, I, and Au) onto the BSCCO surface, and measured changes in the neutralization of scattered Na^+ resulting from the electronic perturbation caused by the adsorbates. Iodine adsorption raises the surface work function, and the neutralization of scattered Na^+ decreases accordingly. It can thus be concluded that the local potential at the Bi sites is increased by the presence of the I adatoms. On the other hand, it is found that although K adsorption decreases the surface work function, it does not effect the neutralization of ions scattered from surface Bi. Au adsorbates appear to coalesce and form clusters on the Bi-O surface, similar to its behavior on other oxide materials [15, 16].

We performed density functional theory (DFT) calculations of the clean surface and with I and K adsorbates in order to determine the preferred adsorption sites and the expected local work functions. In addition, DFT enabled an estimate of the “freezing distance”, beyond which charge exchange does not occur, to be $\sim 2 \text{ \AA}$ from the outermost Bi layer. (These calculations were done in collaboration with Prof. Ruqian Wu from UC Irvine.)

The high-symmetry adsorption sites were identified by DFT to be the surface hollow site for I, and atop a surface O atom for K. For both of these low symmetry sites, DFT predicts that the potential at the surface Bi atoms would be altered from that of the clean surface. Thus, a change in neutral fraction in alkali scattering from Bi is expected for both I and K, despite the fact that it is seen only for I.

In order to reconcile the difference between the measurements and the calculations, we propose that I does adsorb at the low symmetry site, while K does not. For K, it is concluded that the adsorption occurs at step edges and/or other defects. This is consistent with reports of alkali adsorption on other materials, in which case the adatoms often form atomic chains, or “nanowires” [17]. We plan to follow up this work

with scanning probe measurements to investigate this hypothesis.

We also measured the effects of ion bombardment on the surface structure. Spectra collected as a function of Ar^+ sputtering fluence reveal a disorder-induced change in the spectra, indicating that the corrosion-resistant surface does not erode in a layer-by-layer fashion. We performed numerical simulations of the ion scattering process to show how the ions act to reveal the deeper layers. This finding may offer an alternative explanation to the work function changes that have been seen in SIMS studies of this material [13].

These experiments are currently being written up and will be published shortly.

2) Kondo effect. It has been proposed that the Kondo effect can be demonstrated with a noble metal by using the impinging ion as the impurity [18, 19]. The impinging ion needs to have a single unpaired electron, so that singly ionized alkaline earth elements are preferred. The experiments involve measuring the temperature dependence of the charge exchange. Normally, neutralization in systems that undergo RCT increases with increasing temperature, but the neutralization would instead decrease in the presence of the Kondo effect.

We began the experiments with Ca^+ ions, but found that K^+ contamination in the ion beam was too difficult to remove. We next tried Mg^+ , but found that the ions were completely neutralized so that temperature-dependent changes could not be measured. We have now settled on using Sr^+ ions, which do not have these issues.

In order to collect good statistics, we used a clean Au foil in UHV and bombarded it with Sr ions until its work function has reached a saturation value. In this manner, the measurements become insensitive to further beam damage.

As the temperature is raised above room temperature, the neutral fraction initially increases, but it reaches a maximum at about 600°C and then decreases with additional heating. This decrease in neutralization with temperature may be indicative of the Kondo effect. More data is being collected to confirm this result. In addition, we are trying to improve the signal-to-noise in our spectrometer so that we could measure the clean Au foil before any Sr contamination is introduced.

The results will be compared to theoretical predictions in the literature, as well as to experimental results from similar systems that are not expected to display the Kondo effect. From these measurements, the utility of ion scattering to probe the Kondo effect will be conclusively demonstrated. These results will be written up and published shortly.

3) Conventional superconductivity. This was the most risky of the experiments, as the superconducting gap is too small to be easily imaged by ion scattering, and the correlation length is long so that superconductivity may not extend to the surface. Nevertheless, if there were a measurable change in neutralization as a function of temperature, this technique would then provide a means for testing nanoscale films of materials for their electronic properties.

As a first test, we scattered Na^+ ions from a rough Niobium (Nb) foil, as it is the conventional superconductor with the highest T_C , and measured charge exchange probabilities as a function of temperature. No correlation with temperature was found in this initial trial, but it is possible that this is due to the inability to completely clean the surface of polycrystalline Nb. Work in the literature has shown that the only way to get a clean Nb surface is to employ a single crystal. The next step will therefore involve cleaning a single crystal Nb surface.

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